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Characterization of polymer inclusion membrane containing Aliquat 336 as a carrier

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Abstract. The presented research is about characterization of Cellulose Triacetate (CTA) based Polymer Inclusion Membranes (PIMs) which incorporated the commercial extractant Aliquat 336, Tributylphosphate (TBP) as modifier and 2-Nitro Phenyl Pentyl Ether (NPPE) as plasticizer, for the preparation of the membranes. Chemical and physical characteristics of the synthesized membranes especially membrane thickness and side difference effects were investigated. Different surface structures and membrane thickness affect the extraction efficiency of membranes. Membrane extraction experiments were studied where the glass-facing surface of the membranes placed next to feed phase and the air-facing surface to stripping phase. The membrane was characterized by means of AFM, FT-IR and SEM.

Keywords: characterization; polymer inclusion membrane; air-facing surface; glass-facing surface

1. Introduction

In recent years, membrane-based processes have attracted significant attention as a valuable technology for many industries. It is possible to find a lot of applications in the literature and some of those applications were summarized by Ng *et al*. (2013), Tres *et al*. (2010), Farrell and Sirkar (2001). Polymeric membranes have many advantages, such as easy forming properties, selectively transfer of chemical species and one of the very important one as Nghiem *et al*. (2006) were reported is being environmentally friendly.

The rate of metal ion transport through polymer inclusion membrane (PIMs) is arguably a decisive factor influencing the commercialization of this technology. Not surprisingly, most of the PIM studies available to date have reported on this crucial parameter, although often not in a consistent form.

Transport in both PIMs and supported liquid membrane (SLMs) is governed by a number of factors including the membrane morphology, membrane composition solution chemistry in the source and receiving phases as well as the temperature. Because many aspects of PIMs remain unclear at this stage, interpretation and comparison of the current literature data will require a careful consideration of the experimental conditions involved (Nghiem *et al*. 2006).

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Konczyk *et al*. (2010), created a PIM system that used Aliquat 336 as a plasticizer and removed Cr (III) using D2EHPA as the carrier. For that study, CTA, TBP and Aliquat 336 presented a basis for the formation of a polymer inclusion membrane.

Transport through PIMs can be strongly influenced by the membrane morphology. The membrane surface roughness is also an important morphology parameter. Wang *et al*. (2000) reported a slight but discernible increase in metal ion transport when the rougher side of the PIMs was exposed to the source solution.

Imaging with field emission SEM (FESEM) is a standard method for the investigation of perforated materials. AFM is a scanning probe microscopy technique that allows investigating surface properties and features by measuring atomic interactions between a surface and a small tip while a scanning process occurs, creating a high-resolution image. Another important application of AFM is force spectroscopy, the direct measurement of tip-sample interaction forces as a function of the gap between the tip and sample in a vertical displacement. For this method, the AFM tip is extended towards and retracted from the surface while the cantilever deflection is monitored as a function of piezoelectric displacement (Barbosa and Silva 2012). This approach gives information about nano roughness of surface and relationship being between filtration efficiency tests, along with their chemical composition. In order to characterize the surface characteristics quantitatively, highlighting the relations concerning to the structural and chemical differences among them and to filtration performances Fourier transform infrared spectroscopy (FTIR) was utilized.

2. Experimental

2.1 Preparation of PIM

PIM membranes were prepared according to casting solution. First, cellulose triacetate (480 mg) dissolved in 70 mL of dichloromethane and 2-NPPE was added in it, which was dissolved at room temperature. In addition Aliquat 336 and TBP were added to this mixed which was followed of mixing in order to a reach a uniform solution. Then it was allowed to stand overnight this solution a glass square container (24 cm × 24 cm) because of evaporate the solvent of mixed solution at a slow rate. Later this process, distilled water were placed and washed on the top of the polymer film. It was observed that the polymer film obtained has an average thickness of 25 μm, which measured by a digital micrometer (Salu Tron Combi-D3).

2.2 Permeation experiments

The permeation experiments using cobalt and nickel were carried out according to carrier diffusion. Permeation using mixtures of cobalt/nickel solutions were carried out in a glass container using a membrane with area of 12.56 cm^2. This container has a two compartment and was made pyrex glass. In the latter module, mixtures of 100 ppm cobalt and nickel solutions and ammonium tiocyanate (NH_4SCN, 0.5 M) were used in the feed solution. Mixtures of 1M NH_3 + 1M TEA were used in the stripping solution. The feed phase pH was 4 and the temperature was 20°C. The duration of the extraction experiment was 5 hours.

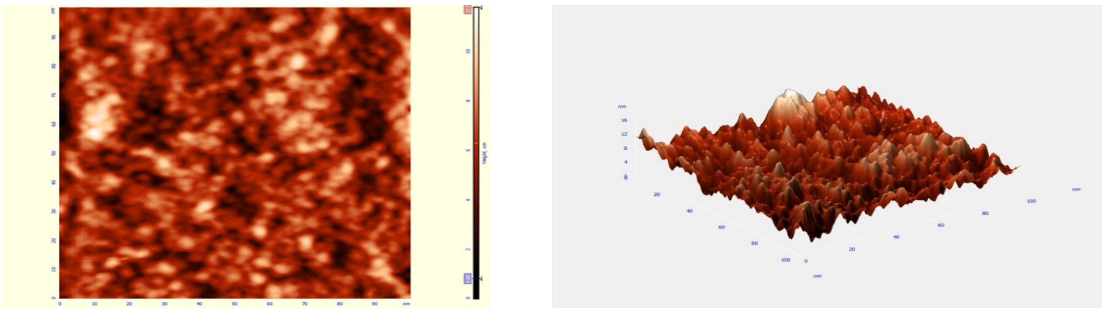
3. Results and discussion

3.1 Membrane characteristics

Microstructure of the membrane materials, which determine allocation of carriers in the polymer matrix and membrane transport adeptness, is important for the PIM system. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are two of the most common surface characterization techniques used in such studies. SEM and AFM studies regularly conclude that polymeric composition has an exceptional influence on membrane morphology.

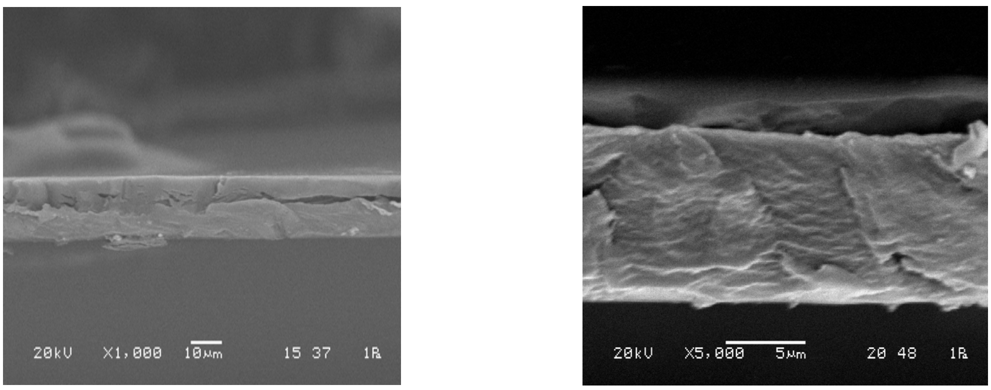
AFM (Fig. 1), SEM (Fig. 2) and FT-IR (Fig. 3) were used to characterize the membrane. The constructed membranes' surface morphology was characterized by the AFM technique. Fig. 1 illustrates the AFM picture of PIM formed by CTA + NPPE + TBP + Aliquat 336. The morphology of membrane has a rough surface nature. Kozlowski and Walkowiak (2005), Tor *et al*. (2009) claim that these surface areas may be caused by different solvent vaporization rates or pores within the membranes that were filled by NPPE + Aliquat 336 + TBP (Ulewicz *et al*. 2010, Kebiche-Senhadji *et al*. 2008).

SEM and AFM techniques are flexible and do offer useful visual information about the



(a) (b)

Fig. 1 AFM picture of PIM formed by CTA + NPPE + TBP + Aliquat 336



(a) (b)

Fig. 2 SEM picture of PIM formed by CTA + NPPE + TBP + Aliquat 336

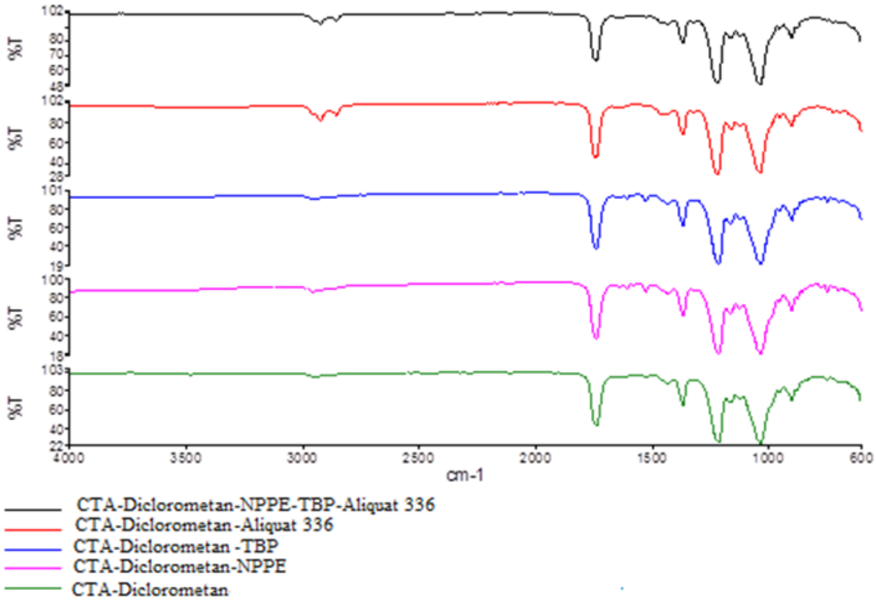


Fig. 3 ATR-IR spectrum of PIM membrane

membrane's surface, and moderately, the membrane's interior structure (Adelung *et al*. 2012) Studies that have used these techniques, up to this point, have not yet been able to explain clearly and in a detailed manner the characteristics of carrier and plasticizer distribution within the membrane.

FT-IR studies showed that all the membrane constituents persisted as pure components within the membrane (Fig. 3).

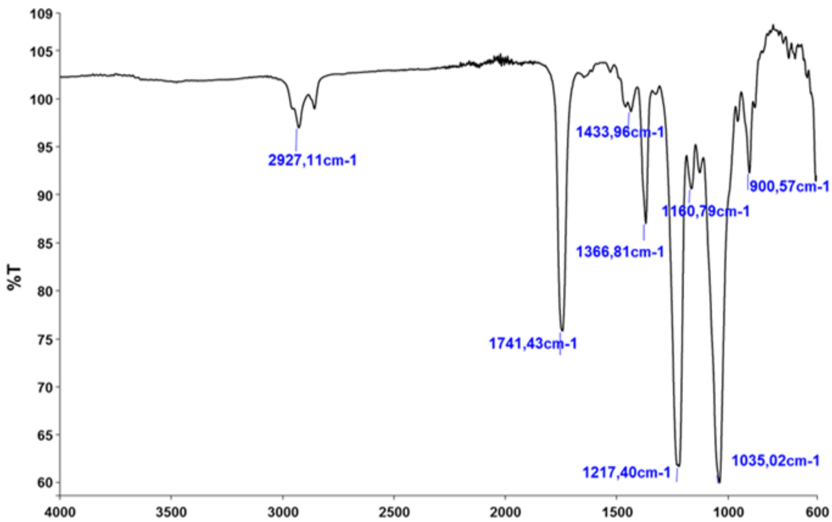


Fig. 4 Glass facing side of membrane before experimental run

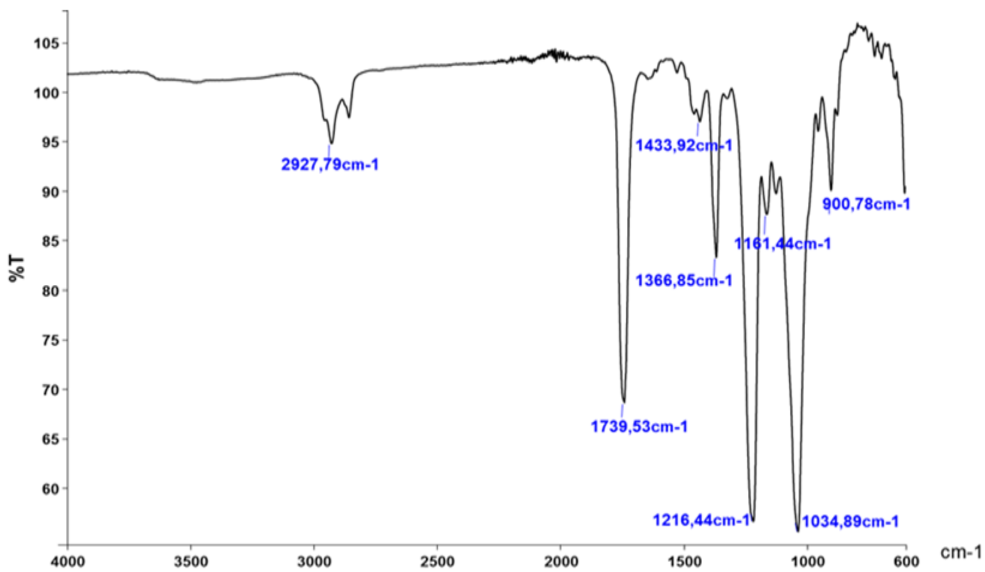


Fig. 5 Air facing side of membrane before experimental run

3.2 Effect of the different sides of the membrane

It was observed that the extraction of Co (II) by two sides (feed phase-stripping phase) of the Aliquat 336/CTA membrane was not the same. The forming conditions of the two sides of the membrane were not identical. When a membrane is prepared, one surface is in contact with glass and the other with the air surface (Figs. 4 and 5).

Wang *et al*. (2000) were shown that there are differences between both sides of membranes poured on a glass surface. As it is expected, glass surface of membrane appears smoother than the

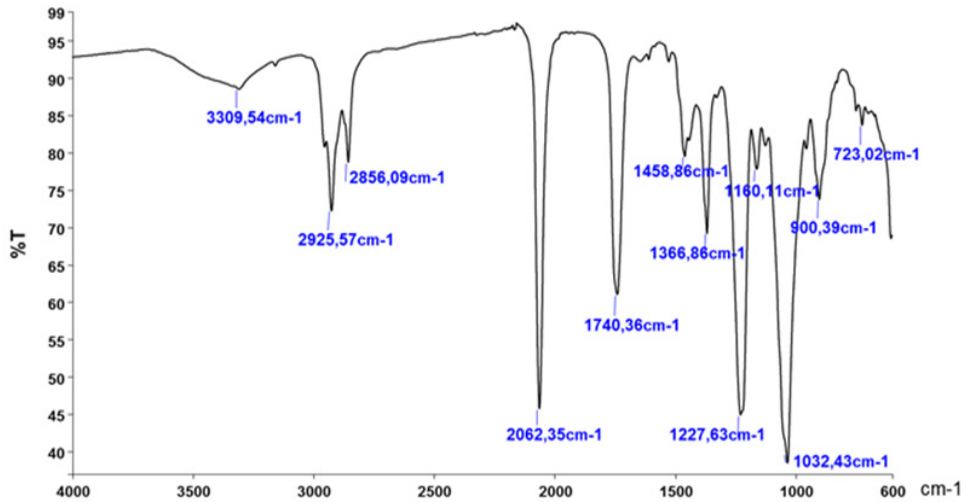


Fig. 6 Glass facing side of membrane after experimental run

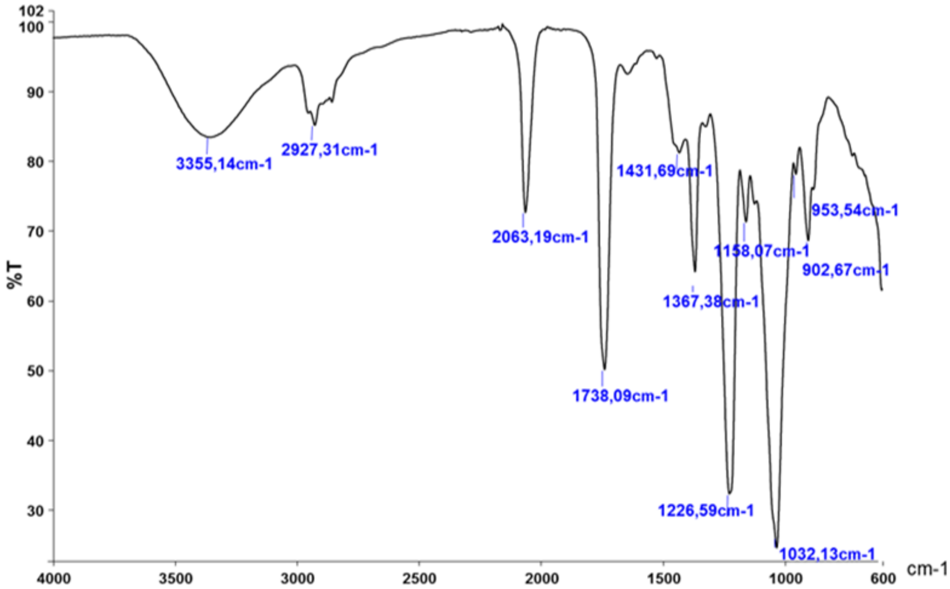


Fig. 7 Air facing side of membrane after experimental run

air surface of membrane. Membrane surface was investigated before and after extraction process by FT-IR. After extraction, PIM membrane spectra showed a new band appeared at 2,062 cm^{-1} due to SCN^- (Figs. 6 and 7).

3.3 Effect of the membrane thickness on the extraction

Membrane thickness was examined for 25, 35, 45, 60 and 110 μm respectively (Fig. 8). It was observed that an increase in the membrane density was followed by a decrease in the extraction. The equation that expresses the metal ions' recovery factor (η) from the feed phase to stripping phase is Eq. (1)

$$\eta = \frac{C_1 - C}{C_i}.100\% \tag{1}$$

Where c is a metal ion concentration in a feed phase at some given time, and c_i is the initial metal ion concentration in the feed phase.

The permeation coefficient (P) and initial flux (J_o), from C-t curves, were calculated from Eqs. (2)-(3)

$$\ln\frac{C}{C_o} = -\frac{A}{V_F}.P.t \tag{2}$$

$$J_o = -\left(\frac{dc}{dt}\right)_o \left(\frac{V_F}{A}\right) \tag{3}$$

Where V_F is the volume of the feed phase, C and C_o are the concentrations of cobalt in the feed

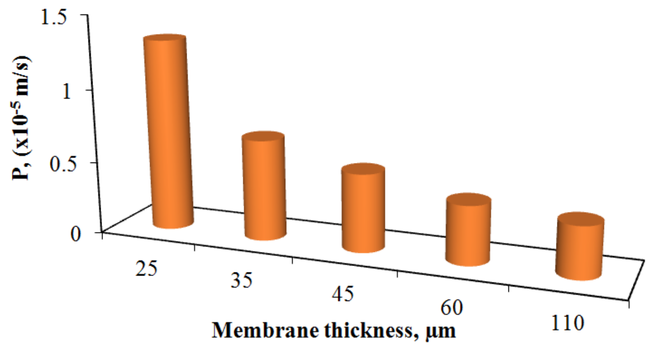


Fig. 8 Effect of the membrane thickness on cobalt permeation coefficient

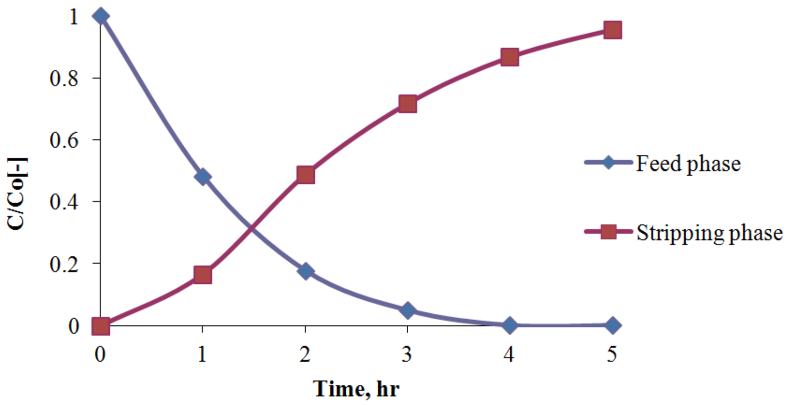


Fig. 9 The extraction efficiency of feed and stripping phase (Feed phase concentration: 100 ppm; Stripping solution: 1M NH_3 + 1M TEA; Feed stripping speed: 900 rpm; Stripping phase stirring speed: 900 rpm; NH_4SCN concentration: 0.5 M; Feed phase volume: 250 mL; Strip phase volume: 250 mL; pH: 4)

phase at elapsed time and time zero, respectively, and t is the elapsed time.

$\left(\frac{dc}{dt}\right)_o$ is the slope at $t = 0$, A is the membrane area.

Membrane extraction experiments were studied where the glass-facing surface of the membranes placed next to feed phase and the air-facing surface to stripping phase. For the equimolar feed mixtures the extraction efficiency was obtained 95.7% in the stripping phase while in the feed phase 100% within 5 hour (Fig. 9).

4. Conclusions

Polymer inclusion membrane was prepared using Aliquat 336, TBP and 2-NPPE. FT-IR studies showed that all the membrane constituents persisted as pure components within the membrane. Effect of the membrane thickness on the permeation coefficiency was investigated in the acidic mixture of cobalt and nickel solutions. For 25 μm membrane thickness the permeation coefficiency was obtained 1.32 × 10^{-5} in the feed phase. The prepared polymer showed good extractive properties for Co (II) ions and the extraction efficiency was calculated 100% in the feed phase.

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